

Design and characterization of carbon nanotube nanocomposites

Emilie J. Siochi, Peter T. Lillehei, Kristopher E. Wise*, Cheol Park* and Jason H. Rouse*

Advanced Materials and Processing Branch
NASA Langley Research Center
Hampton, VA 23681

*National Institute of Aerospace
Hampton, VA 23666

ABSTRACT

Revolutionary design concepts in future aerospace vehicles will depend on extraordinary material properties to permit significant reduction of mass and size of components, while imparting intelligence. Due to their combination of remarkable electrical and mechanical properties, carbon nanotubes (CNT) are expected to enable this paradigm shift in design concepts. However, significant challenges still exist in translating these CNT properties into the macrostructures required for future generations of aerospace vehicles. While an accepted route for making the leap from nanostructures to useful macrostructures has not been fully charted, this paper will give an overview of the approach taken by some researchers at NASA Langley Research Center to sort out issues involved in the development of CNT nanocomposites for multifunctional structures. Specifically, the dispersion of carbon nanotubes in polymer matrices, characterization of nanocomposites, the role of quantum computation in providing guidance for processing and the use of computational analysis in data interpretation will be covered. Significant improvements in mechanical and electrical properties of CNT nanocomposites with very low loadings of CNTs are described and lend credence to the potential for using CNTs in achieving technological leaps in composite development.

Keywords: Carbon nanotubes, nanocomposites, microscopy, mechanical properties, electrical properties, computation and modeling.

1. INTRODUCTION

Ambitious goals to improve aircraft technology while reducing costs and minimizing environmental impacts require radical departures from existing vehicle design concepts [1]. From the materials perspective, efficient vehicles with reduced life cycle costs can be enabled by the incorporation of multifunctional structures. State-of-the-art structures use graphite fiber composites to achieve weight reduction without sacrificing mechanical properties. However, while graphite fiber composites satisfy the weight

reduction requirements, they do not depart from their primary utility as load bearing structures. In contrast to graphite fibers, carbon nanotubes (CNT) possess the mechanical properties to enable the necessary weight reduction, as well as superior electrical properties [2]. This suggests that they can be used to replace graphite fiber in load bearing structures and impart sensing capability as well, thus producing a multifunctional structure.

Carbon nanotubes are graphene cylinders and single wall nanotubes (SWNT) typically have diameters of about 1 nm with lengths ranging from several microns to tens of centimeters [3,4]. In contrast to graphite fibers which are typically processed into prepreg as a precursor to composite structures, it is not clear at this point how the leap from carbon nanostructures to macro composite structures is to be made. This is due in part to some unique problems with carbon nanotubes. While nanotubes have great affinity for each other, the formation of high stiffness and strength, long fibers analogous to graphite fibers remains elusive. Nevertheless, due to their attractive combination of mechanical and electrical properties, efforts to develop methods that take advantage of CNTs' potential to enable multifunctional structures continue. Ultimately, the most compelling case for CNTs replacing graphite fibers in multifunctional structures will be made based on properties that the nanocomposites deliver.

Several papers have been published by the Biologically Inspired Smart Nanotechnology (BIOSANT) research group at NASA Langley Research Center (LaRC) on the topic of CNT nanocomposite development [5-8]. The objective here is to provide an overview of the approach used by the BIOSANT research group to overcome obstacles in CNT nanocomposite fabrication and ultimately to evaluate their potential in multifunctional structures. These challenges include homogeneously dispersing CNTs in a polymer matrix and characterizing the quality of the nanocomposites. In both of these endeavors, computation and modeling have played a significant role in determining which experimental parameters to study, as well as interpreting experimental observations.

2. FACTORS AFFECTING CARBON NANOTUBE DISPERSION

2.1 CNT dispersion method

Two methods of CNT dispersion were investigated. The first method, designated as direct mixing, involved predispersing CNTs in dimethylformamide (DMF) by homogenization followed by sonication, then addition to a polyimide solution by stirring. The second method is in-situ polymerization. In this case, the pre-dispersed CNTs were incorporated into a polyimide matrix during polymerization. Details of both methods are documented elsewhere [5].

The dispersion method used affects the quality of nanocomposite films significantly. Better distribution of the CNTs was achieved by in-situ polymerization compared to direct mixing. This is evident in the optical micrographs shown in Figure 1 for polyimide films doped with 1vol% CNT; more clumping of the carbon nanotubes was clearly visible in the nanocomposite film when direct mixing was the dispersion method. The insets in Figure 1 also show that film transparency was affected by dispersion quality. The nanocomposite film obtained by direct mixing was much darker and transmitted less than 1% light at 500 nm wavelength compared to the film fabricated by in-situ polymerization which had 32% transmission at the same wavelength [5]. This finding is significant in applications where transparency is an important consideration.

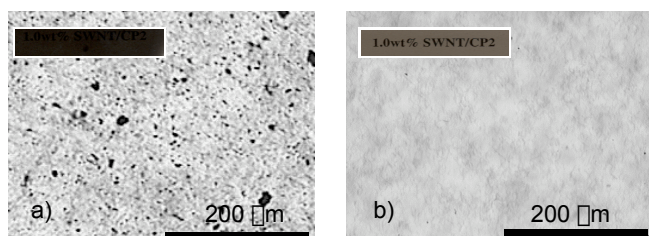


Figure 1. Effect of dispersion method on dispersion quality and light transmission a) Direct mixing b) In-situ polymerization.

2.2 Polymer matrix chemistry

The two polyimides chosen for this investigation were LaRC CP2 and (4-CN) APB/ODPA. Synthesis methods for these materials are documented elsewhere [9,10]. Their chemical structures are shown in Figure 2.

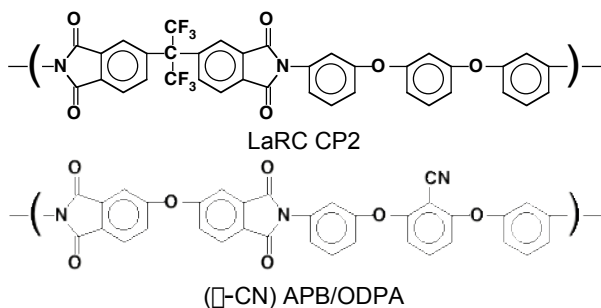


Figure 2. Chemical structures of polyimides used

Quantum computational modeling predicted favorable interaction between the cyano functional groups on (4-CN) APB/ODPA and the surface of CNTs [11]. This interaction is not present in LaRC CP2 polyimide.

2.3 Characterization of CNT nanocomposites

2.3.1 Microscopy of CNT nanocomposites

Using the scanning electron microscope (SEM) as a tool to visualize the CNTs in polymer matrix composites involves an understanding of the phenomena responsible for contrast in electron microscopy. SEM uses a scanning electron beam to generate secondary electrons from a sample surface. The probability that a sample location will generate a secondary electron is dependent upon a number of factors, most notably the conductivity and temperature of the sample. Since CNTs are both very good electrical and thermal conductors, their presence in the composite will reduce the probability of generating a secondary electron at the surface of the polymer, yielding dark regions in the nanocomposite image. SEM was extremely useful for discerning variations in dispersion homogeneity for composite samples that appeared similar under optical microscopy. Figure 3 shows film surface and cross-section images of CP2/SWNT and (4-CN)/SWNT composites both at 1vol% loading of SWNT. The two samples appear similar at the surface, however, the SEM images in cross-section revealed that there was greater aggregation in the LaRC CP2 nanocomposite compared to the (4-CN) APB/ODPA nanocomposite, indicating better dispersion in (4-CN) APB/ODPA. Both nanocomposites were prepared via in situ polymerization, but (4-CN) APB/ODPA was predicted to have tighter binding to the nanotube surface. This has implications in electrical conductivity where efficiency of dispersion can determine the percolation threshold. Better dispersed CNTs may result in lower conductivity percolation thresholds due to more effective electron transport through the bulk sample.

2.3.2 Mechanical and electrical properties of CNT nanocomposites

Doping polyimide matrices with carbon nanotubes at loading levels ranging from 0.1 to 1.0% by volume has been shown to yield dramatic improvements in both electrical and mechanical properties. Specifically, for LaRC CP2, a ten order of magnitude increase in volume conductivity was realized at the percolation threshold of 0.05% CNT loading. This percolation threshold was consistent with the model of carbon nanotubes homogeneously dispersed into bundles of one to seven nanotubes [7]. This increase in electrical conductivity made the nanocomposite a suitable material for electrostatic charge dissipation in space applications [5].

Similar dramatic increases in mechanical properties were measured for LaRC CP2 as well. At 1% by volume of CNT doping, a 65% increase in storage modulus compared to undoped CP2 was observed [5]. This dramatic increase in mechanical property at such low doping levels was not consistent with the rule of mixtures and points to unusual behavior at the nanoscale having significant impacts on bulk properties.

3. SUMMARY AND CONCLUSIONS

Although there is great potential for the development of the next generation of polymer matrix composites which take advantage of the impressive suite of properties possessed by carbon nanotubes, there are significant challenges yet to be overcome. In this paper, it was demonstrated that taking advantage of the combination of electrical and mechanical properties of carbon nanotubes for the development of multifunctional structures is possible when the fundamental

problems of chemical interactions and characterization method development are approached with the aid of computation and analytical modeling. Improved electrical and mechanical properties obtained for nanocomposites containing very low concentrations of carbon nanotubes demonstrate that there is promise in the translation of excellent properties at the nanoscale to useful bulk structures with improved properties compared to state-of-the-art materials.

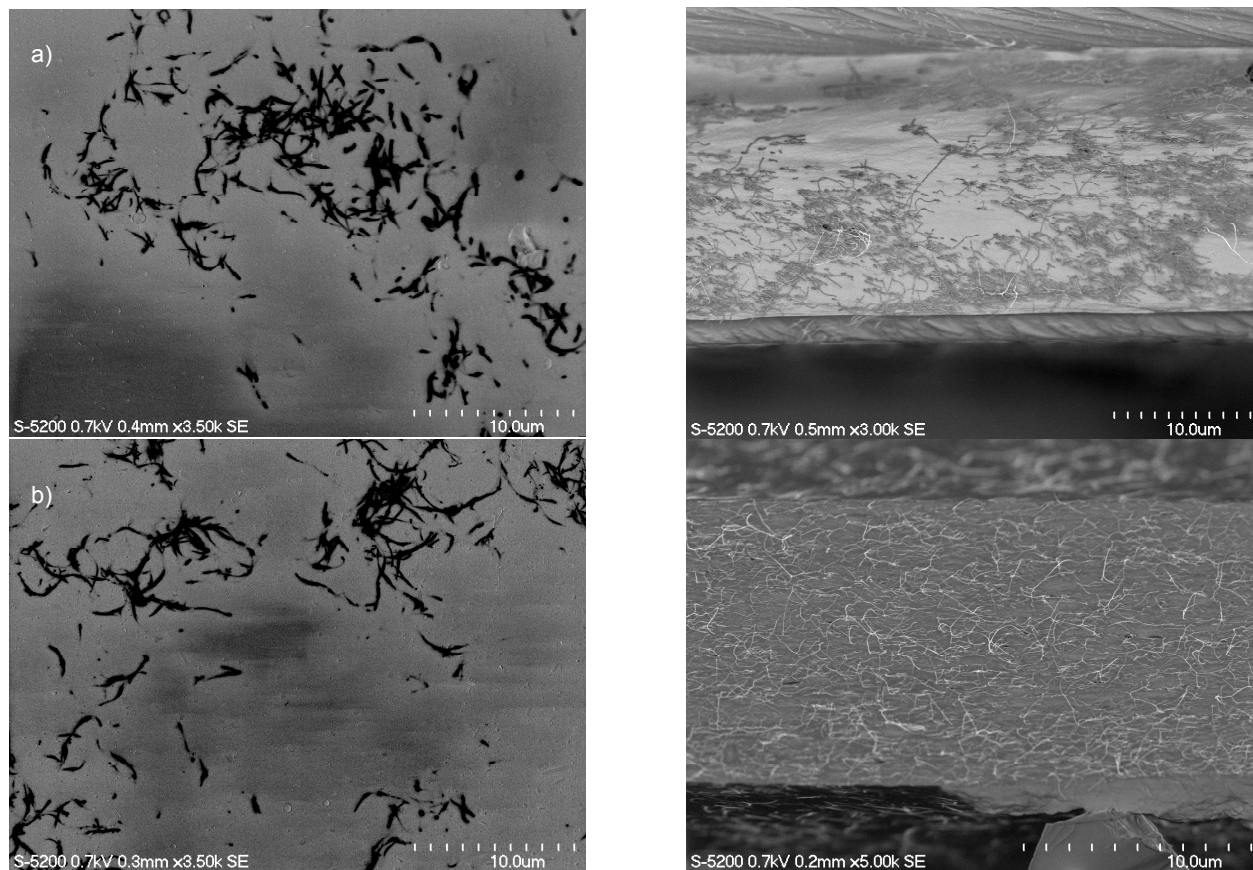


Figure 3. Film and cross-sectional scanning electrical micrographs of in situ polymerized a) CNT/LaRC CP2 b) CNT/(□-CN) APB/ODPA.

4. REFERENCES

- [1] National Aeronautics and Space Administration 2003 Strategic Plan, <http://www.nasa.gov>.
- [2] P. M. Ajayan, "Nanotubes from carbon," *Chem. Rev.* 99: 1787-1799, 1999.
- [3] H. M. Cheng, F. Li, X. Sun, S. D. M. Brown, M. A. Pimenta, A. Marucci, G. Dresselhaus and M. S. Dresselhaus, "Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons," *Chem. Phys. Lett.* 289: 602-610, 1998.
- [4] H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtal, and P. M. Ajayan, "Direct synthesis of long single-walled carbon nanotube strands," *Science*, 296: 884-886, 2002.
- [5] C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, J. Smith, Jr., S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison and T. L. St. Clair, "Dispersion of single wall carbon nanotubes by in-situ polymerization under sonication," *Chem. Phys. Lett.*, 364: 303-308, 2002.
- [6] P. T. Lillehei, C. Park, J. H. Rouse and E. J. Siochi, "Imaging carbon nanotubes in polymer composites via magnetic force microscopy," *NanoLetters*, 2: 827-829, 2002.
- [7] Z. Ounaies, C. Park, K. E. Wise, E. J. Siochi and J. S. Harrison, "Electrical properties of single wall carbon nanotube reinforced polyimide composites," *Composites Sci. and Technol.*, 2003, in press.

- [8] C. Park, R. E. Crooks, E. J. Siochi, N. Evans and E. Kenik, "Adhesion of polyimide to single wall carbon nanotube bundles revealed by energy filtered transmission electron microscopy," submitted to *Chem. Phys. Lett.*
- [9] A. K. St. Clair and T. L. St. Clair, "Process for preparing highly optically transparent colorless aromatic polyimide films," U. S. Patent 4,603,061, 1986.
- [10] J. Simpson, Z. Ounaies and C. Fay, "Polarization and piezoelectric properties of a nitrile substituted polyimide," *Mat. Res. Soc. Symp. Proc.*, 459: 53-55, 1997.
- [11] K. E. Wise, C. Park and E. J. Siochi, "Donor acceptor stabilization of polymer carbon nanotube composites," in preparation.
-